

Magnetism of Substitutional Co Impurities in Graphene: Realization of Single π -Vacancies

E. J. G. Santos,* D. Sánchez-Portal,[†] and A. Ayuela[‡]

Centro de Física de Materiales, Centro Mixto CSIC-UPV/EHU, Apdo. 1072, 20080 San Sebastián, Spain and Donostia International Physics Center (DIPC), Paseo Manuel de Lardizabal 4, 20018 San Sebastián, Spain

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We report *ab initio* calculations of the structural, electronic and magnetic properties of a graphene monolayer substitutionally doped with Co (Co_{sub}) atoms. We focus in Co because among traditional ferromagnetic elements (Fe, Co and Ni), only Co_{sub} atoms induce spin-polarization in graphene. Our results show that, nearby the Fermi energy, the electronic structure of substitutional Co is equivalent to that of a vacancy in a π -tight-binding model of graphene. Additionally, we investigate the magnetic coupling between several Co_{sub} . We find that the total spin moment of arrays of Co_{sub} defects depends on the Co occupation of A and B graphene sublattices, in accord with the Lieb's theorem for bipartite lattices. The magnetic couplings show more complex behaviors.

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The peculiar electronic and magnetic properties of graphene monolayers have recently attracted much attention.^{1,2,3,4} New types of electronic and, particularly, spintronic devices based on graphene have been proposed. These graphene structures have also driven an increasing interest to study defects, which are always expected in real-life devices. Intrinsic defects have been already widely studied^{4,5,6,7,8} and extrinsic defects, like substitutional atoms, are presently under intense research.^{9,10,11,12} Recently, Gan *et al.*¹³ using high-resolution transmission electron microscopy (HRTEM) have observed substitutional Au and Pt atoms in graphene monolayers. They observed large activation energies for in-plane migration, which point towards strong covalent carbon-metal bonding and high stability for such substitutional defects. In spite of the growing interest about defects in graphene, little is known on magnetic properties, such as spin polarizations and couplings, for the traditional bulk magnets Fe, Co and Ni placed substitutionally in graphene.

In this work, we present a study of the structural, electronic and magnetic properties of substitutional Co (Co_{sub}) atoms in a graphene monolayer. We show that Co has spin polarization. This is in contrast to Fe and Ni substitutions which surprisingly do not show spin polarization¹⁴. We observe that there is a one-to-one correspondence between the expected behavior for single vacancies in a simple π -tight binding model of graphene and that found for the Co_{sub} defects. The Co atom stabilizes a symmetric structure of the carbon vacancy. The electronic structure of the Co_{sub} defect at the Fermi energy (E_{Fermi}) is dominated by a single level with a strong contribution from the p_z orbitals of the neighboring C atoms. Each Co_{sub} defect shows a spin moment of $1.0 \mu_B$. The total spin, however, follows closely Lieb's theorem for bipartite lattices¹⁵ and depends on the number of Co substitutions in each sublattice. Thus, magnetic couplings are predominantly (anti)ferromagnetic for Co_{sub} defects sited in the (opposite) same sublattice. Our calculations also show the dependence of the couplings on the crystalline direction and relative position of the de-

fects.

We have used the SIESTA code^{16,17} for our calculations. We have checked that the norm-conserving pseudopotential¹⁸ used for Co satisfactorily reproduces the band structure and spin moment of bulk Co. The pseudopotential includes nonlinear core corrections¹⁹ for exchange and correlation, with a pseudo-core matching radius of 0.67 a.u. Computational parameters guarantee the convergence of relative energies for different magnetic configurations within the meV.¹² The results obtained with VASP code^{20,21}, using a well converged plane-wave cutoff of 400 eV and the projected-augmented-wave scheme, are almost identical to those obtained with SIESTA.

The relaxed geometry and the magnetization density for a Co_{sub} defect in a graphene monolayer is given in Fig. 1(a). The Co atom appears displaced 0.92 Å from the carbon surface, and it has a symmetrical three-fold coordinated structure with Co-C distances of 1.77 Å. The three C-Co-C bond angles are quite similar and have a value $\sim 97^\circ$. The binding energy of the Co atom to the carbon vacancy in graphene is 7.6 eV. In comparison, the most stable adsorption configuration of Co on graphene has a much lower energy of 1.3 eV. Therefore, Co_{sub} defects are likely to be found in carbon nanostructures synthesized using Co-containing catalysts, as seems to be the case for Ni²². Furthermore one could expect that Co_{sub} defects can be fabricated in a controlled way by creating vacancies in graphene and subsequently depositing Co. The presence of Co_{sub} defects could be detected today by scanning tunneling microscopy (STM)²³, X-ray adsorption techniques²² and HRTEM¹³.

Figure 1 (a) shows the spin-polarization pattern induced by the presence of a Co_{sub} impurity. The spin polarization induced in the neighboring carbon atoms has a clear p_z -like shape. The sign of the spin polarization follows the bipartite character of graphene: the polarization aligns parallel (antiparallel) to the spin moment of the Co impurity for carbon atoms sitting in the opposite (same) sublattice than the Co atom. The total spin

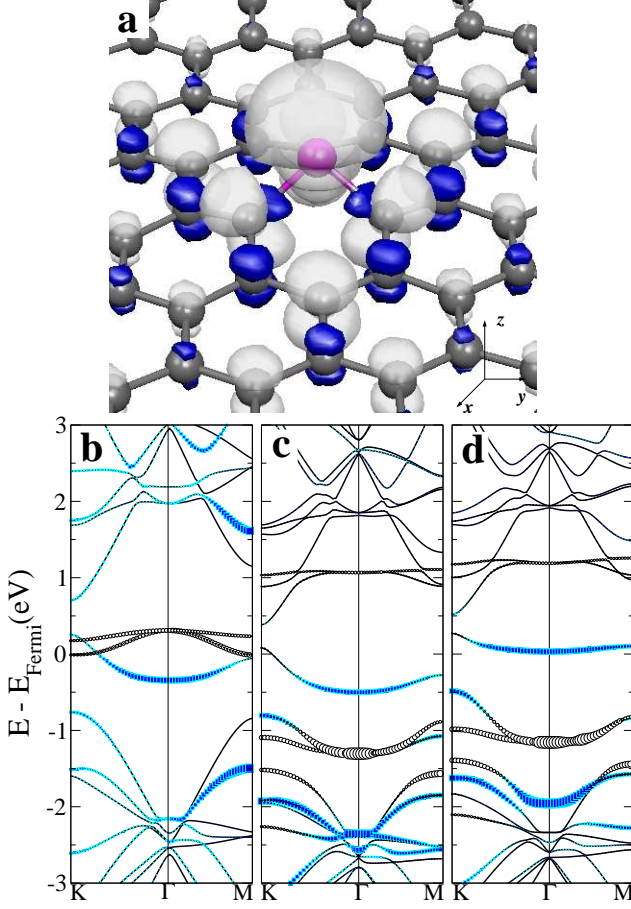


FIG. 1: (Color online) (a) Isosurface of the spin density induced by a Co_{sub} defect. Positive and negative spin densities correspond to light and dark surfaces with isovalues of $\pm 0.008 \text{ e}^-/\text{Bohr}^3$, respectively. Panel (b) presents the spin-unpolarized band structure of an unreconstructed carbon vacancy. Panel (c) and (d) show, respectively, the majority and minority spin band structure a Co_{sub} defect in a similar cell. Filled symbols in panel (b) indicate the contribution of the p_z orbitals of the C atoms surrounding the vacancy, whereas empty symbols correspond to the sp^2 character. In panels (c) and (d), filled and empty circles denote the contribution of hybridized Co 3d_{z²}-C 2p_z and Co 3d-C 2sp² characters, respectively. E_F is set to zero.

moment is $1.0 \mu_B$. Using Mulliken population analysis, $0.44 \mu_B$ are assigned to the Co atom; $0.20 \mu_B$, to the three first carbon neighbors; and $0.36 \mu_B$, delocalized in the rest of the layer. The spin polarization decays with distance very slowly.

To understand the origin of this spin polarization, we now analyze in detail the band structure of this system. Figures 1 (c) and (d) present the results for a Co_{sub} defect in a 4×4 graphene supercell. Similar results are obtained using an 8×8 cell. For comparison, the panel (b) shows the spin-compensated band structure of a single unreconstructed carbon vacancy, the so called D_{3h} vacancy.⁶ For the D_{3h} vacancy, three defect states appear in a range of $\sim 0.7 \text{ eV}$ around the Fermi energy (E_F).

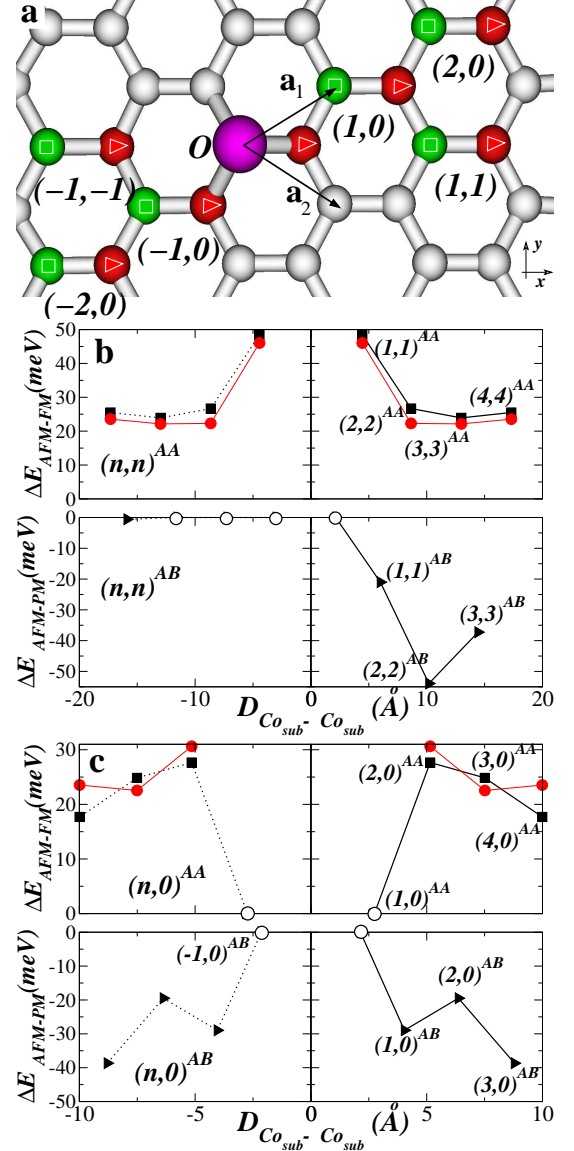


FIG. 2: (Color online) (a) Schematic representation of the geometry used to calculate the relative stability of ferromagnetic (FM), antiferromagnetic (AFM) and spin compensated (PM) solutions as a function of the positions of two Co_{sub} impurities. Sublattices A and B are indicated by squares and triangles, respectively. One of the impurities is fixed in a central A-type site, whereas the other is moved along the (b) (n,n) and (c) $(n,0)$ directions. The empty circles represent spin compensated solutions and the full circles correspond to a fit with a Heisenberg model (see text).

Two states appearing at 0.3 eV above E_F at Γ have a large contribution from the sp^2 lobes of the C atoms surrounding the vacancy. Other state at 0.35 eV below E_F at Γ shows a predominant p_z contribution. The p_z level corresponds with the defect state that appears pinned at E_F for a vacancy in a simplified π -tight-binding description of graphene.

When a Co atom is bound to the vacancy, the defect

states described above hybridize with the 3d states of Co. The two $2sp^2$ defect bands, now an antibonding combination of Co 3d and the original C $2sp^2$ vacancy levels, are pushed at higher energies, ~ 1.0 eV above E_F (see Fig. 1 (c) and (d)). The singly occupied p_z state, now hybridized mainly with the Co $3d_{z^2}$ orbital, remains pinned at the E_F and becomes almost fully spin-polarized. Thus, the Co_{sub} impurities becomes analogous to a π vacancy. The splitting between majority and minority p_z defect bands is ~ 0.50 eV. The spin splitting is much smaller for all other bands.

We consider next the magnetic couplings between Co_{sub} defects in a large 8×8 supercell with two Co_{sub} impurities. We calculate the energy difference between different spin alignments as a function of the relative position of the defects. Figure 2 shows the results along with a schematic representation of our notation. These energies are comparable to the spin-flip energies in ferromagnetic transition metals Fe, Co and Ni. Several observations can be made: (i) when the impurities are located in the same sublattice (AA systems) the ferromagnetic (FM) configuration is more stable than the antiferromagnetic (AFM) one; (ii) if the Co atoms are in opposite sublattices (AB systems) it is very difficult to reach a FM solution,²⁴ instead the system finds either a spin-compensated (PM) or an AFM solution; (iii) at short distances (< 3.0 Å) the systems always converge to spin compensated solutions.

In the FM cases, the total spin magnetization integrates to $2.00 \mu_B$, with a spin population on every Co atom that remains almost constant $\sim 0.50 \mu_B$ ($\sim 0.30 \mu_B$ for the three C-nearest neighbors). In other cases the total spin is zero. Thus, the total magnetic moment of the system follows the equation $S = |N_{\text{sub}}^A - N_{\text{sub}}^B|$, where $N_{\text{sub}}^{A(B)}$ is the number of Co_{sub} defects in the A(B) sublattices. Therefore, our total moment is consistent with Lieb's theorem for bipartite lattices¹⁵. This supports our analogy between the electronic structure of Co_{sub} defects and single vacancies in a simplified π -tight-binding description of graphene.

The spin magnetization density for some selected configurations is plotted in Fig. 3. Although the spin is fairly localized on the Co atom and the neighboring C atoms, the presence of the defect also causes a delocalized magnetization density with alternated signs in the two sublattices. The triangular pattern, that reflects the three-fold symmetry of the layer, shows different orientations for A and B substitutions. This explains the very anisotropic AB interaction along the (n, n) direction seen in Fig. 2 (b): the energy difference between AFM and PM solutions for $(n, n)^{AB}$ configurations strongly depends on the relative position of the impurities, showing such directionality. Similar patterns have already been observed experimentally^{25,26,27,28} in point defects (e.g. vacancies and hydrogens) on graphene by means of STM techniques and also theoretically discussed for π -vacancies.^{10,29,30} For Co_{sub} in graphene, similar STM experiments should display the topology of the spin densities given in Fig. 3.

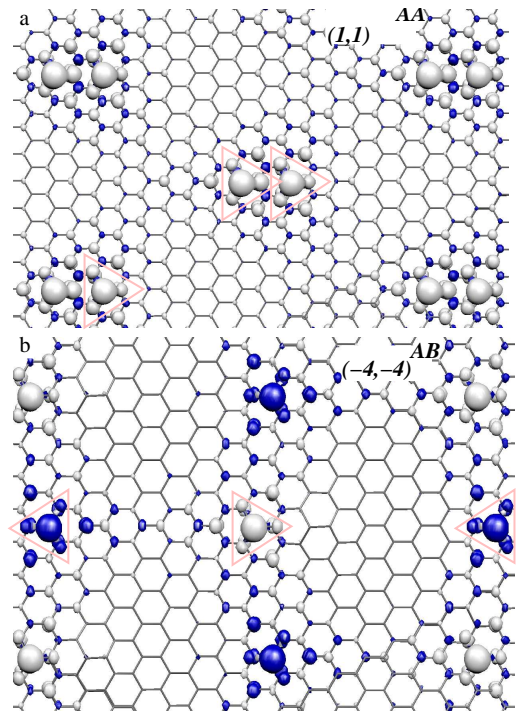


FIG. 3: (Color online) (a) Spin densities for configurations (a) $(1,1)^{AA}$, and (b) $(-4,-4)^{AB}$ (see Fig. 2(a) for the nomenclature). Positive and negative spin densities are indicated by light (gray) and dark (blue) isosurfaces corresponding to $\pm 0.001 \text{ e}^-/\text{Bohr}^3$, respectively.

We have also investigated the magnetic interactions within the framework of a classical Heisenberg model, $H = \sum_{i<j} J_{AA/AB}(\mathbf{r}_{ij}) \mathbf{S}_i \mathbf{S}_j$, where \mathbf{S}_i is the local moment for a Co_{sub} impurity at site i . The expression for the \mathbf{r}_{ij} dependence of the exchange has been taken from analytical RKKY coupling given in Ref. 31, except for the exponent of the distance decay, which is fitted to our *ab initio* results. The exchange interaction for AA systems can be fitted with a $|r_{ij}|^{-2.43}$ distance dependence (see the full circles in Fig. 2 (b) and (c)). This distance dependence is in reasonable agreement with the $|r_{ij}|^{-3}$ behavior obtained with analytical models for substitutional defects and voids^{31,32}. In the case of AB systems a simple RKKY-like treatment fails to satisfactorily describe the interactions, at least for the relatively short distances between defects considered in our calculations.

Next, we explain the appearance of PM solutions in Fig. 2. The appreciable interaction between defect levels in neighboring impurities for AB systems opens a *bonding-antibonding* gap in the p_z defect band³³ and, thus, contributes to the stabilization of PM solutions. For AA systems, however, the bipartite character of the graphene lattice makes the interaction between defects much smaller. This explains the prevalence of solutions showing a local spin polarization for AA configurations. For very short distance between impurities, a larger defect-defect interaction opens a large gap and, in consequence, stabilizes PM configurations. It is interesting to

point out that similar behaviors were previously observed for vacancies in graphene and graphene ribbons described within a simplified π -tight-binding model.^{29,30,34}

Similar behaviors to Co_{sub} are expected for any other system that can be mapped into a simple π -vacancy in graphene. This is the case of a hydrogen atom saturating a C p_z state in graphene.^{35,36} However, there are two important differences between these two systems. As Co prefers energetically to sit on carbon vacancies, Co_{sub} defects could be fabricated by depositing Co atoms on areas where vacancies have been previously created by, for example, electron irradiation or Ar ion bombardment. The calculated diffusion barrier of hydrogen on graphene is 1.19 eV,³⁷ the experimentally observed activation energy for the migration of substitutional metals, such as Au and Pt, in graphene is around 2.5 eV.¹³ Thus, the diffusion is also probably much slower for Co_{sub} defects than for hydrogen atoms. We expect that stable arrays of Co_{sub} impurities could be fabricated and open a route to obtain in reality many of the interesting magnetic be-

haviors obtained for π -models of defective graphene.

In summary, only Co substitutional atoms in graphene respect to other traditional ferromagnetic materials, such as Fe and Ni, present spin polarization. The electronic structure of Co_{sub} defects (see Fig. 1) is dominated by an impurity level at E_F with strong contribution from the p_z states of the neighboring C atoms, and it is a clear reminiscent of a single vacancy in a simplified π -tight-binding description of graphene. The study of the Co coupling in several sites demonstrates FM alignments for the AA cases, in contradistinction to AB cases which are either AFM or spin compensated. The AA cases were fitted to a Heisenberg model with a RKKY exchange constant. Our findings for Co_{sub} can be used to bring into contact the engineering of nanostructures with the results of π -models in defective graphene.

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- * Electronic address: eltonjose.gomes@ehu.es
† Electronic address: sqbsapod@ehu.es
‡ Electronic address: swxayfea@ehu.es
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